# Green Bay Urban Air Toxics Monitoring

## A Summary Report for the Period
## July 1995 - June 1996

# Green Bay Urban Air Toxics Monitoring

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## Executive Summary

The Clean Air Act Amendments of 1990 define an approach to Hazardous Air Pollutants (HAPS) which includes seeking a substantial reduction in emissions and public health risks associated with exposures.  As a part of this, a research program is outlined which includes ambient monitoring for a broad range of HAPs in a representative number of urban locations.

The Wisconsin Urban Air Toxics Monitoring Network (WUATM) was conceived in response to these directives.  The full network was originally planned to consist of 4 or 5 monitoring stations located throughout the state.  A single prototype site was established in Green Bay during 1991. Funding for additional sites has yet to be appropriated.

The initial monitoring was designed to be a screening program to determine concentrations of organic and inorganic compounds present in Wisconsin's urban air.  The program is considered to be a screening program because only a limited number of compounds have been collected and quantified.   Most of these compounds are listed in Table 1 below.  In general, the compounds can be grouped as semi-volatile organic compounds (including polynuclear aromatic hydrocarbons, PCBs and pesticides), polar organic compounds (formaldehyde and phenols), volatile organic compounds and non-volatile metals.

The air toxics monitoring network is intended to provide information for the following uses:

- ► Determine concentrations of HAPs in Wisconsin's Urban Atmospheres
- ► Assess Potential Air Toxics Problems
- ► Background Data and Trend Analysis
- ► Fate of Air Toxics

The prototype site in Green Bay has the additional purpose of evaluating various sampling and analytical methodologies.

The monitoring site was established along the Fox River in Green Bay in March 1993 and remains there at this time.  This report is summarizes results from July 1995 through June 1996, and to make recommendations concerning the continuation and expansion of the toxics monitoring network.  An initial report covering the data from July 1991 through June 1995 has been recently published (publication number AM-218-97)

PAHs as a compound class are among the most studied of the air toxics.  As such, results from around the world are available for comparison.  Total determined PAH values between July and December 1995 ranged from 2.8 to 47.1 nanograms per cubic meter (ng/m$^3$) with an average of

14.7 ng/m$^3$. In January 1996, the parameter list was expanded to include additional compounds. Total determined PAH values through June 1996 ranged from 7.4 to 76.7 ng/m$^3$, with an average of 32.5 ng/m$^3$. An average yearly total PAH value reported for Los Angeles is 10.9 ng/m$^3$. Values in Green Bay between July 1991 and June 1995 ranged from 1.5 to 249.8 ng/m$^3$, with an average of 22.5 ng/m$^3$.

Polychlorinated biphenyl (PCB) and pesticide samples were collected, with PCB values ranging from 0.04 ng/m$^3$ to 2.15 ng/m$^3$, with an average of 0.47 ng/m$^3$. Improvements in sampling and analytical protocols led to an increase in the rate of detection, with PCBs detected in 92.6% of samples submitted. Overall detection for the previous 4 years of this study was 20.5%. Additionally, DDE, dieldrin, cis- and trans- chlordane, trans-nonachlor and lindane were all detected during the 1995/1996 sampling season.

Formaldehyde values in Green Bay range from 0.10 ug/m$^3$ (0.09 ppbv) to 18.45 ug/m$^3$ (15.04 ppbv), with an average of 1.62 ug/m$^3$ (1.32 ppbv). Formaldehyde is monitored elsewhere in the state as part of the Photochemical Assessment Monitoring (PAMS) program. Average values from Milwaukee are comparable to those from Green Bay, in addition to those from studies located in other states.

A variety of volatile organic compounds considered Toxics have been detected in the atmosphere of Green Bay. Detected values have ranged from 0.1 ppbv to 7.3 ppbv (maximum value for acetylene). The average values for all parameters other than acetylene and toluene are less than 1 ppbv (average acetylene value is 3.2 ppbv; average toluene value is 1.0 ppbv). Where overlap exists between the PAMS and the Toxics VOC lists, comparisons between Milwaukee and Green Bay are possible and indicate generally similar concentrations of various parameters. Although VOC concentrations tend to be highly variable based on location, values obtained in other published air toxic studies are generally in the same order of magnitude as those found in Green Bay.

A suite of 6 metals (arsenic, cadmium, chromium, lead, selenium and vanadium) have been well characterized at the Green Bay sites. Average detected values are 1.14 ng/m$^3$, 0.77 ng/m$^3$, 3.46 ng/m$^3$, 12.97 ng/m$^3$, 1.12 ng/m$^3$, and 1.64 ng/m$^3$, respectively. These values are comparable to those obtained in other urban air toxic studies and with previous years in Green Bay.

In summary, the toxics monitoring prototype site in Green Bay provides a significant quantity of information regarding a number of toxic compounds present in the air of this city. Current results can be compared to results obtained during the previous years to provide insight into trends and distribution of HAPS. Ample opportunity has been available for the evaluation of methods used to collect and analyze trace components of the atmosphere.

During the most recent monitoring period, a number of method changes have been made to improve detection limits and consistency of results. Some of these changes include lengthening the winter PCB sampling period from 72 to 144 hours, expanding the parameter list for PCBs and

PAHs, and improving the analytical detection limits for PCBs. Additional work remains to be done in improving the methods in use and expanding the toxics monitoring program.

Recommendations regarding continued operations and expansion of the toxics monitoring network fall into two basic categories: further refinements of methods, and expanding the network to different localities. Several of the methodology changes documented later in this report are already being implemented as this report nears completion.

The original intention of the program was to install permanent sites in 4 or 5 cities around the state. As it currently stands there is not funding available for such an ambitious expansion. However, there are ways in which toxics data from other locales can be generated without the large expense of installing new fixed site monitors. One possibility is to simply relocate the site to another urban area. Also, a combination of rotation of samples between other existing sites for TSP metals and remotely sampling for semi-volatile and volatile organic compounds using portable samplers would be an inexpensive way to help locate toxic hot spots and gather data from other parts of the state.

**Table 1: Parameter List for Wisconsin Urban Air Toxics Monitoring Program**

| | | |
|---|---|---|
| 3-METHYL CHOLANTHRENE | LINDANE | PROPENE |
| ANTHRACENE | TOTAL PCBS (Aroclor) | BENZENE |
| BENZ (A) ANTHRACENE | cis-CHLORDANE | XYLENES (m & p) |
| BENZO ALPHA PYRENE (BAP) | cis-NONACHLOR | 1,1,1-TRICHLOROETHANE |
| CHRYSENE | trans-CHLORDANE | METHYLCHLORIDE |
| CORONENE | trans-NONACHLOR | 1,1,2,2-TETRACHLOROETHANE |
| FLUORANTHENE | ARSENIC | o-XYLENE |
| NAPHTHALENE | CADMIUM | ETHYLBENZENE |
| PERYLENE | CHROMIUM | CHLOROFORM |
| PHENANTHRENE | LEAD | STYRENE |
| PYRENE | SELENIUM | 1,3 BUTADIENE |
| ATRAZINE | VANADIUM | n-OCTANE |
| TECHNICAL CHLORDANE | TSP (ug/M3) | TETRACHLOROETHENE |
| DDE | ACETALDEHYDE | CHLOROETHANE |
| DDT | ACETONE | CARBON TETRACHLORIDE |
| DIELDRIN | FORMALDEHYDE | TRICHLOROETHENE |
| HEPTACHLOR EPOXIDE | ACETYLENE | CUMENE (i-PROPYLBENZENE) |
| HEXACHLOROBENZENE | TOLUENE | 1,4-DICHLOROBENZENE |

# Sampling and Analytical Procedures

Sampling and analytical procedures for all parameters are specified in the Hazardous Air Contaminants Fixed Urban Site Monitoring Program Quality Assurance Project Plan (QA 8.0) prepared by DNR personnel in 1991. Specific methods are documented in the DNR Air Monitoring Handbook.

**Semi-Volatile Organic Compounds: Polynuclear Aromatic Hydrocarbons (PAHs)**

PAH samples are collected using a General Metal Works PS-1 sampler loaded with a combination quartz filter and PUF plug, following EPA TO-13 protocols as outlined in DNR OP 8.5, Sampling Semivolatile Organic Compounds Using a PS-1 Sampler. Air is drawn through the sampler at a rate of approximately 8 cubic feet per minute (CFM) for a period of 24 hours. The sample is then packed in hexane rinsed aluminum foil and shipped to the laboratory for analysis.

Analysis for these parameters is performed at the Wisconsin Occupational Health Laboratory (WOHL). PUF plugs and filters are extracted with 5% ethyl ether/hexane and brought to a final volume of 3 mls. The sample is analyzed by high performance liquid chromatography (HPLC) with a fluorescence detector to determine the presence of selected PAH's.

**Semi-Volatile Organic Compounds: Polychlorinated Biphenyls and Pesticides (PCBs)**

PCB samples are collected using a General Metal Works PS-1 sampler loaded with a combination quartz filter and PUF plug, following EPA TO-4 protocols as outlined in DNR OP 8.5, Sampling Semivolatile Organic Compounds Using a PS-1 Sampler. Air is drawn through the sampler at the maximum possible rate. This rate varies from slightly over 8 CFM to as much as 9.5 CFM, depending upon the condition of the sampler motor.

The initial sampling protocol called for a 72 hour sampling period. This was changed for winter months in November 1995 to a 144 hour period because of a lack of results under the shorter sampling time. The 144 hour sampling period was acheived through 2 separate 3 day sampling periods following the every 12 day sampling schedule. The samples were stored at about $4^{\circ}$C inside their original sampling heads with the ends sealed using Parafilm between the sampling periods. Summer and fall protocol remained with the 72 hour sampling period.

Following collection of the sample, the filter and PUF plug are packed in hexane rinsed aluminum foil and shipped to the laboratory for analysis. Analysis for these parameters is performed at the State Lab of Hygiene (SLOH). PUF plugs and filters are extracted with 5% ethyl ether/hexane and brought to a final volume of 1 ml. The extracts are analyzed by gas chromatography with an electron capture detector to determine the presence of selected chlorinated compounds. Confirmation of compounds is through the routine use of dual column analysis, with occassional mass spectroscopy.

## Polar Organic Compounds:  Carbonyls

Carbonyl samples are collected by drawing a known volume of ambient air through commercially prepared cartridges containing 2,4-dinitro phenylhydrazine (DNPH) coated silica gel, following EPA TO-11 as outlined in DNR OP 8.4, Aldehyde Sampling with 2,4-Dinitro phenylhydrazine impregnated sampling cartridges.  Aldehydes react with the DNPH to form stable derivatives which can then be analyzed.  Samples are collected over a 24 hour period at a rate of approximately 700 cc/min.  Following collection, samples are refrigerated until shipment to the laboratory.

Aldehyde samples are analyzed at WOHL.  The exposed cartridges are washed with acetonitrile to remove the aldehyde-DNPH derivatives.  The eluant is brought to a known volume and then analyzed by reversed phase HPLC coupled with UV absorption detection.

## Volatile Organic Compounds

Sampling and analysis of VOCs follows the protocols of EPA TO-14 employing passivated stainless steel canisters.  A low flow 24 hour sample is collected in an evacuated canister, which is then sent to the laboratory for cryogenic concentration followed by high resolution gas chromatography with mass spectroscopic detection.  The analysis is performed at Biospheric Research Corporation in Hillsboro, Oregon.

## Total Suspended Particulate and Metals

Standard high volume methods as documented in DNR OP.1.2, High Volume Sampler, are employed at the Green Bay Toxic monitoring sites for the collection of TSP samples.  A 24 hour sample is collected on a pre-weighed glass fiber filter at an average flow rate of 1.42 $m^3$ per minute.  Filters are sent to the SLOH for determination of total mass of particulate collected.  The same sample is used for determination of ambient concentrations of non-volatile metals.  The metals are determined by digesting a portion of the filter in acid and analyzing the resulting solution using atomic absorption spectroscopy.

## Quality Assurance Objectives

Several aspects of quality control and assurance protocols have been incorporated into the monitoring program in Green Bay.  The quality assurance objectives are precision, accuracy, completeness, representativeness and comparability.

Precision for discrete samples is determined by means of quarterly duplicate samples.  The goal is for the duplicates to be within ±15% for each individual parameter.

Accuracy is intended to be determined on two levels, that of sampling using air flow audits, and also analytical accuracy through submission of spiked samples.  Sampler audits are performed yearly by personnel other than the regular site operator, with the goal being to have the actual

flow rate within ±10% of the expected sampling air flow rate.

Analytical relative accuracy determinations are made by submitting samples spiked with representative compounds. These samples are occasionally available from EPA and other sources. Several of these samples were submitted. In addition, spiked media recovery determinations are a typical part of the analytical in-house quality control mechanism. The goal for accuracy determinations are for the results to be within ±25% of the actual amount introduced to the media.

The completeness parameter involves trying to obtain valid samples for all scheduled sampling days. Monitoring plans call for sampling metals every 6 days. All other parameters were sampled on an off-set every 12 days schedule.

Representativeness is accomplished through meeting the criteria for sampling locations set forth by USEPA in the Compendium of Methods for the Determination of Toxic Organic Compounds and 40 CFR Part 58, Appendix E. Comparability involves reporting data in units consistent with other organizations reporting similar data. In general, volatile compounds are reported in part per billion volume (ppbv), while semi-volatile and non-volatile compounds are reported in micrograms or nanograms per cubic meter (ug/m$^3$ or ng/m$^3$).

# Results

## Polynuclear Aromatic Hydrocarbons, Data Completeness

PAH samples were collected throughout the year. There were no significant periods of lost samples for any reason. In addition to the regularly scheduled ambient and QC samples, several extra QC samples were obtained, including spiked samples and alternative sampling materials submitted for blank determinations.

Sampling and analytical completeness with reference to PAHs is documented in the following table. Sampling completeness relates the actual samples collected as documented by field sheets on record to the number of sampling days in each period. In this application, Completeness is the ratio of Ambient samples collected to total Sampling days. Analytical Completeness in the ration of Samples to Samples Submitted.

**Table 2: Polynuclear Aromatic Hydrocarbon Completeness**

| Sampling Completeness | Samples | Voids | Ambient | Blanks | Spikes | Duplicates | Sample Days |
|---|---|---|---|---|---|---|---|
| 100.0% | 43 | 2 | 30 | 5 | 2 | 4 | 30 |

| Analytical Completeness | Samples | Ambient | Blanks | Spikes | Duplicates | Samples Submitted |
|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |

| 102.4% | 42 | 32 | 5 | 2 | 3 | 41 |
|---|---|---|---|---|---|---|

The current value for sampling completeness represents an improvement over the overall project sampling completeness of 64.0% (between July 1991 and June 1995), and continues the trend established during the first half of 1995. The analytical completeness value reflects the accidental submission of a void ambient sample for analysis. It should be noted that this sample was void because the final time was not filled in on the data sheet. Calculations of sample volume and subsequent results were based on an assumed final time of 1440 minutes (24 hours).

## Polynuclear Aromatic Hydrocarbons, Analytical Results

The table following represents summation of all samples. Evaluation criteria are average, maximum, and minimum reported values, along with percent relative standard deviation. Results of all samples were calculated on the basis of maximum possible values in the case of non-detects, and actual values in the case of detected quantities. Additional reporting criteria include the number of detects, how many samples reported each particular parameter, and the % Detection, based on the ratio of detects to total samples. Results are reported as ng/cubic meter.

**Table 3: Polynuclear Aromatic Hydrocarbon Results (ng/m$^3$)**

| Parameter Name | Average | Maximum | Minimum | % RSD | Detects | Reported | % Detection |
|---|---|---|---|---|---|---|---|
| 3-METHYL CHOLANTHRENE | 0.02 | 0.12 | 0.01 | 170.9% | 8 | 14 | 20.5% |
| ANTHRACENE | 0.52 | 1.56 | 0.08 | 87.1% | 19 | 20 | 48.7% |
| BENZ (A) ANTHRACENE | 0.97 | 2.27 | 0.03 | 60.4% | 19 | 20 | 48.7% |
| BENZO ALPHA PYRENE (BAP)* | 0.02 | 0.17 | 0.01 | 154.7% | 11 | 32 | 28.2% |
| CHRYSENE* | 0.03 | 0.24 | 0.01 | 165.3% | 3 | 26 | 7.7% |
| CORONENE | 0.09 | 0.52 | 0.03 | 149.7% | 4 | 16 | 10.3% |
| FLUORANTHENE* | 2.90 | 17.53 | 0.14 | 107.5% | 36 | 38 | 92.3% |
| NAPHTHALENE* | 2.37 | 17.38 | 0.04 | 161.5% | 37 | 39 | 94.9% |
| PERYLENE | 11.43 | 32.76 | 0.44 | 110.3% | 11 | 12 | 28.2% |
| PHENANTHRENE* | 12.95 | 66.56 | 1.73 | 96.7% | 36 | 37 | 92.3% |
| PYRENE | 1.96 | 3.58 | 0.07 | 54.6% | 14 | 17 | 35.9% |

Number of Samples: 30          Number of Blanks: 5          Number of Duplicates: 4

The table above represents parameters reported numerically by the laboratory. It should be noted that mid-way through the period documented in this report, the parameter list was expanded from 5 to 11 compounds. Parameters marked with an asterix (*) represent compounds which were part of the official parameter list throughout the year. Additionally, the laboratory did not report all requested parameters for every sample.

These values are consistent with those obtained in this study previously, with no new maximum or minimum values.

## Polynuclear Aromatic Hydrocarbons, Quality Assurance Parameters

Results of duplicate and blank samples are documented below.  It should be noted that not a single duplicate passes QC criteria of ±25% for all parameters.  For the purposes of this data, a bad pair indicates that one sample was a detect, while the other was not for a particular parameter.  A total of 2 bad data pairs were obtained out of 24 total data pairs, indicating that 91.7% of the data pairs were acceptable on this level.   Of the 22 good data pairs, 16 (66.7) represent detect pairs (where both results show results), while 6 (25.0%) represent non-detect pairs.  Only pairs with at least one detect are included in the table.

Overall average percent differences between the good data pairs is  ±29.7%, with 5 (of 22, or 22.7%) of the pairs showing a difference of greater than ±25%.  Average percent differences for the good pairs are ±6.8% for Anthracene,  ±4.3% for Benzo (a) Anthracene,  ±17.8% for Benzo (a) Pyrene, ±8.1% for Chrysene,  ±8.8% for Coronene,  ± 72.8% for Fluoranthene,  ± 32.6% for Naphthalene, ±7.5% for Phenanthrene and  ±95.1% for Pyrene.  Although these results show some improvement over previous years, it remains a cause of concern.   All duplicate results are shown graphically on the following page.

**Table 4: Polynuclear Aromatic Hydrocarbon Duplicates (ng/m$^3$)**

| Parameter Name | Date | Primary | Duplicate | Average | % Diff | Detects |
|---|---|---|---|---|---|---|
| 3-METHYL CHOLANTHRENE | 05/21/96 | 0.01 | 0.01 | 0.01 | 63.0% | Y/N |
| ANTHRACENE | 03/10/96 | 0.11 | 0.10 | 0.10 | 13.6% | Y/Y |
| ANTHRACENE | 05/21/96 | 0.85 | 0.85 | 0.85 | 0.1% | Y/Y |
| BENZ (A) ANTHRACENE | 03/10/96 | 0.58 | 0.55 | 0.56 | 6.0% | Y/Y |
| BENZ (A) ANTHRACENE | 05/21/96 | 1.50 | 1.54 | 1.52 | 2.6% | Y/Y |
| BENZO ALPHA PYRENE (BAP) | 03/10/96 | 0.02 | 0.02 | 0.02 | 37.0% | Y/Y |
| FLUORANTHENE | 12/05/95 | 1.15 | 0.87 | 1.01 | 27.5% | Y/Y |
| FLUORANTHENE | 03/10/96 | 1.55 | 1.51 | 1.53 | 3.1% | Y/Y |
| FLUORANTHENE | 05/21/96 | 0.14 | 4.32 | 2.23 | 187.8% | Y/Y |
| NAPHTHALENE | 12/05/95 | 0.15 | 0.26 | 0.21 | 55.4% | Y/Y |
| NAPHTHALENE | 03/10/96 | 0.36 | 0.43 | 0.39 | 18.1% | Y/Y |
| NAPHTHALENE | 05/21/96 | 1.68 | 2.14 | 1.91 | 24.2% | Y/Y |
| PERYLENE | 05/21/96 | 1.49 | 2.32 | 1.91 | 43.2% | Y/Y |
| PHENANTHRENE | 12/05/95 | 1.95 | 2.27 | 2.11 | 15.3% | Y/Y |
| PHENANTHRENE | 03/10/96 | 5.23 | 5.44 | 5.34 | 3.9% | Y/Y |
| PHENANTHRENE | 05/21/96 | 29.67 | 30.68 | 30.17 | 3.3% | Y/Y |

| PYRENE | | 03/10/96 | 1.37 | 1.37 | 1.37 | 0.3% | Y/Y |
|--------|--|----------|------|------|------|------|-----|

# Green Bay Urban Air Toxics
## PAH Duplicate Samples
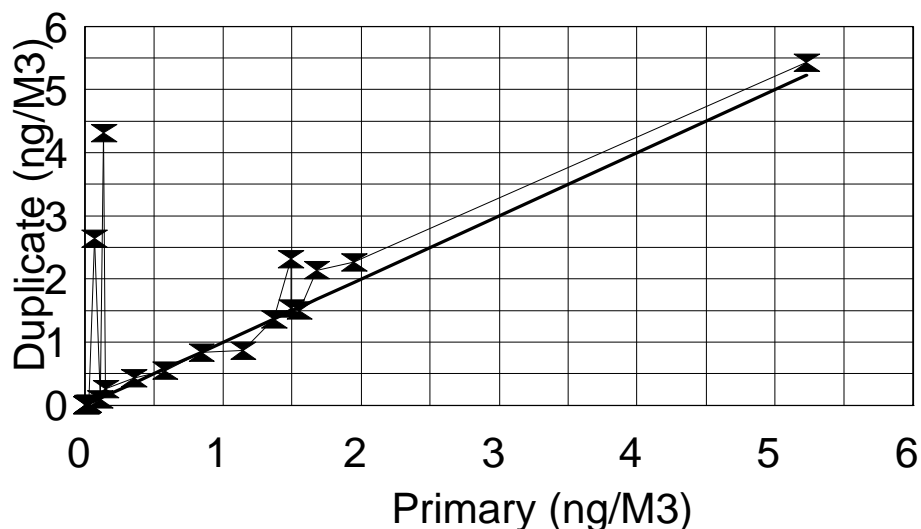


| PYRENE | | 05/21/96 | 0.07 | 2.64 | 1.36 | 190.0% | N/Y |
|--------|--|----------|------|------|------|--------|-----|

Occasional blanks have shown traces of different parameters. These detects have been evaluated at a representative sampling volume (350 cubic meters) to determine the level of potential interference. Many parameters consistently exceed the QC limits of 10 ng per PUF. In addition, some parameters have detection limits above 10 ng/sample.

It should be noted that the Naphthalene value from 01/08/96 (marked with an asterix (*)) derives from the first of a series of tests of XAD resin containing sampling materials. This parameter has shown itself to be exceptionally difficult to obtain clean blanks on. Whether the difficulty lies within the lab or is simply part of the sample matrix is at this time unknown. Only detected parameters are tabulated below. A ⬜<=⬜ sign indicates interference which may or may not be related to the parameter in question.

One significant aspect of the blank values obtained is that 62.5% of the Benzo (a) Pyrene values, 7.7% of the Fluoranthene values, and 46.2% of the Naphthalene values are less than 3 times the average blank. The levels of analytes present in the blanks thus constitutes a major difficulty in evaluating the results obtained from this testing.

**Table 5: Polynuclear Aromatic Hydrocarbons in Blanks**

| Parameter | Date | ng/sample | ng/M3 |
|---|---|---:|---:|
| ANTHRACENE | 01/22/96 | 5 | 0.01 |
| ANTHRACENE | 04/15/96 | <=4.0 | 0.01 |
| BENZ (A) ANTHRACENE | 01/22/96 | 51 | 0.15 |
| BENZ (A) ANTHRACENE | 03/21/96 | 22 | 0.06 |
| BENZ (A) ANTHRACENE | 04/15/96 | 38 | 0.11 |
| BENZO ALPHA PYRENE (BAP) | 10/06/95 | <=5.0 | 0.01 |
| BENZO ALPHA PYRENE (BAP) | 01/22/96 | 10 | 0.03 |
| BENZO ALPHA PYRENE (BAP) | 03/21/96 | <=5.0 | 0.01 |
| BENZO ALPHA PYRENE (BAP) | 04/15/96 | 9 | 0.03 |
| FLUORANTHENE | 01/22/96 | 96 | 0.27 |
| FLUORANTHENE | 04/15/96 | 63 | 0.18 |
| NAPHTHALENE | 10/06/95 | 225 | 0.64 |
| NAPHTHALENE* | 01/08/96 | 418 | 1.19 |
| NAPHTHALENE | 01/22/96 | 474 | 1.35 |
| NAPHTHALENE | 03/21/96 | 111 | 0.32 |
| NAPHTHALENE | 04/15/96 | 165 | 0.47 |
| PHENANTHRENE | 10/06/95 | <=50 | 0.14 |
| PHENANTHRENE | 03/21/96 | <=50 | 0.14 |
| PHENANTHRENE | 04/15/96 | 60 | 0.17 |
| PYRENE | 04/15/96 | 83 | 0.24 |

## Polynuclear Aromatic Hydrocarbons, Analytical Recovery Determination

In addition to the regular array of duplicates and blanks, a spiked series of PUFs was submitted in February 1996. A standard spiking solution was prepared by mixing stock standards from the laboratory. An aliquot of 10 uL of this solution was used to yield the resultant ng/PUF values reported in the table below. A spiked cartridge was submitted directly to the laboratory (referred to as Spiked Blank in the table below) along with a spiked cartridge that was then sampled as a duplicate with an unspiked one, as per the method of standard additions.

Results from this test are reported in the table below. The Recovery  columns are the ratio of Blank and Net to ng/PUF, respectively. The control limit for this determination is ±25%. In other words, the test is considered acceptable if the laboratory reports results which are anywhere between 75% and 125% of the known quantity of material added to the sampling materials. This goal was achieved only with Pyrene, Benzo (a) Pyrene, 3-Methyl Cholanthrene

and Anthracene for both spiked samples.  Phenanthrene and Fluoranthene achieved the recovery goal for the direct determination, but failed for the spiked sample.  Phenanthrene and Naphthalene recovery changes between the two tests suggests the possibility of loss of material over the sampling period which is consistent for use of PUF cartridges without an XAD backup.  Coronene results are extremely consistent between the determinations, although just below acceptable recovery levels.

Chrysene, Perylene, Fluoranthene  and Benzo (a) Anthracene results are highly erratic and suggest identification difficulties present in the laboratory procedures.  An examination of the original chromatograms confirms the presence of overlapping peaks (potentially accounting for the excessively high recovery values noted for some parameters) and peaks shifted outside of their expected retention time windows, thereby remaining unidentified (accounting for the missing Chrysene and Perylene in the spiked blank).

Overall, the spiking tests indicate difficulties in this determination both at the sampling (loss of more volatile compounds) and analytical phases (peak separation and identification difficulties).  It should be noted, however, that several of the less volatile compounds did pass this test, thereby validating their data, at least on this level.

**Table 6: Polynuclear Aromatic Hydrocarbon Spike Recoveries (ng)**

| Parameter | ng/PUF | Spiked Blank | Blank/ng/PUF | Spike | Sample | Net | Net/ng/PUF |
|---|---|---|---|---|---|---|---|
| **Naphthalene** | 6778.2 | 4580 | 67.6% | 4970 | 2080 | 2890 | 42.6% |
| **Phenanthrene** | 5421.8 | 4850 | 89.5% | 10000 | 6480 | 3520 | 64.9% |
| **Fluoranthene** | 363.6 | 335 | 92.1% | 2750 | 1460 | 1290 | 354.8% |
| **Pyrene** | 1242.7 | 1400 | 112.7% | 2130 | 978 | 1152 | 92.7% |
| **Benz a Anthracene** | 224.5 | 800 | 356.3% | 316 | 677 | -361 | -160.8% |
| **Benz a Pyrene** | 1079.1 | 1140 | 105.6% | 1130 | 0 | 1130 | 104.7% |
| **3 methyl cholanthene** | 772.7 | 765 | 99.0% | 711 | 7 | 704 | 91.1% |
| **Anthracene** | 1258.2 | 1120 | 89.0% | 1510 | 353 | 1157 | 92.0% |
| **Chrysene** | 573.6 | | 0.0% | 1360 | 13 | 1347 | 234.8% |
| **Perylene** | 410.0 | | 0.0% | 9750 | 11600 | -1850 | -451.2% |
| **Coronene** | 834.5 | 608 | 72.9% | 603 | 0 | 603 | 72.3% |

## Polychlorinated Biphenyls and Pesticides, Data Completeness

PCB and pesticide samples were collected continuously throughout the testing period.  Based on previous experience with an inability to detect these substances during the winter, extra sensitivity was added to the method by increasing the sampling time from 72 to 144 hours, in addition to decreasing the detection limits in the lab.  Thereafter nearly every sample has had detectable quantities of PCB.  A total of fourteen 144-hour samples and twenty four 72-hour

samples were collected.

In addition to adjusting the method to improve sensitivity, the parameter list for this analysis has been changed. The non-specific technical Chlordane has been dropped in favor of cis- and trans-Chlordane, cis- and trans- Nonachlor, and Heptachlor Epoxide. DDT has been replaced with DDE, and Hexachlorobenzene has simply been dropped. This parameter list change occured in January, 1996, so that the results reported here include some from each analysis regime.

Project completeness is documented in the following table. In this table, Sampling Completeness is the ratio of Ambient samples collected to total Sampling days. Analytical Completeness in this table is the ratio of Samples to Samples Submitted.

#### Table 7: PCB and Pesticides Completeness

| Sampling Completeness | Samples | Voids | Ambient | Blanks | Spikes | Duplicates | Sample Days |
|---|---|---|---|---|---|---|---|
| 91.3% | 38 | 4 | 21 | 4 | 3 | 6 | 23 |
| **Analytical Completeness** | **Samples** | **Ambient** | **Blanks** | **Spikes** | **Duplicates** | | **Samples Submitted** |
| 100.0% | 33 | 20 | 4 | 3 | 6 | | 33 |

## Polychlorinated Biphenyls and Pesticides, Analytical Results

Results of all samples were evaluated on the basis of maximum possible values in the case of non-detects, and actual values in the case of detected quantities. The table below summarizes results for all reported PCB analytical parameters. Values are reported in ng/m$^3$. All PCB results are shown graphically on the following page, along with a line representing the limits of detection under various sampling and analytical regimes.

### Table 8: PCB and Pesticide Results (ng/m$^3$)

| Parameter | Average | Maximum | Minimum | RSD(%) | Detects | Reported | % Detect |
|---|---|---|---|---|---|---|---|
| TOTAL PCBS (Aroclor) | 0.47 | 2.15 | 0.04 | 92.2% | 25 | 27 | 92.6% |
| LINDANE | 0.03 | 0.08 | 0.00 | 71.7% | 11 | 27 | 40.7% |
| DIELDRIN | 0.04 | 0.06 | 0.01 | 49.2% | 5 | 27 | 18.5% |
| DDE | 0.01 | 0.02 | 0.00 | 64.9% | 3 | 14 | 21.4% |
| trans-CHLORDANE | 0.01 | 0.02 | 0.00 | 60.4% | 2 | 14 | 14.3% |
| cis-CHLORDANE | 0.01 | 0.02 | 0.00 | 59.7% | 2 | 14 | 14.3% |
| HEPTACHLOR EPOXIDE | 0.01 | 0.04 | 0.00 | 92.4% | 1 | 14 | 7.1% |
| trans-NONACHLOR | 0.01 | 0.02 | 0.00 | 51.7% | 1 | 14 | 7.1% |
| ATRAZINE | 0.15 | 0.21 | 0.08 | 31.4% | 0 | 27 | 0.0% |
| cis-NONACHLOR | 0.01 | 0.01 | 0.00 | 37.9% | 0 | 14 | 0.0% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **DDT** | 0.05 | 0.05 | 0.02 | 15.0% | 0 | 13 | 0.0% |
| **HEXACHLOROBENZENE** | 0.03 | 0.03 | 0.01 | 15.0% | 0 | 13 | 0.0% |
| **CHLORDANE** | 0.28 | 0.31 | 0.14 | 15.0% | 0 | 13 | 0.0% |

Number of Samples: 23        Number of Duplicates: 4

All parameters with more than 2 and less than 20 detects were also evaluated on the basis of detects only, to provide a clearer picture of what ambient concentrations of these parameters are in this area.  PCBs were not similarly treated because of the high detection rate present.

**Table 9: Pesiticde Results, Detects Only (ng/m$^3$)**

| Detects Only | Average | Maximum | Minimum | % RSD |
|---|---|---|---|---|
| **DDE** | 0.02 | 0.02 | 0.01 | 30.3% |
| **DIELDRIN** | 0.05 | 0.06 | 0.04 | 13.8% |
| **LINDANE** | 0.03 | 0.08 | 0.00 | 79.9% |

As reported in the previous Green Bay Urban Air Toxics Data Report, insufficient data is available for the determination of yearly and seasonal trends in PCB and pesticide concentrations at this time.  This type of analysis may be feasible by the end of 1997.

## Polychlorinated Biphenyls and Pesticides, Quality Assurance Parameters

Duplicate precision is reported for samples wherein detects were noted.  Out of a total of 37 data pairs, there were 2 bad pairs (5.4%), 31 non-detect pairs (83.8%), and 4 detect pairs (10.8%).  It should be noted that in each of the bad pairs, one of the samples was at the detection limit, while the other was just below.  As the table below shows, the relative percent difference between the bad pairs is still less than ±10%.  Only data pairs with at least one detect are tabulated below.

**Table 10: PCB and Pesticide Duplicates (ng/m³)**

| Parameter Name | Primary | Duplicate | Average | % Diff | Detects |
|---|---|---|---|---|---|
| TOTAL PCBS (Aroclor) | 0.89 | 0.85 | 0.87 | 4.5% | Y/Y |
| TOTAL PCBS (Aroclor) | 0.04 | 0.04 | 0.04 | 7.8% | N/Y |
| TOTAL PCBS (Aroclor) | 0.40 | 0.36 | 0.38 | 9.4% | Y/Y |
| TOTAL PCBS (Aroclor) | 0.06 | 0.06 | 0.06 | 3.9% | Y/Y |
| LINDANE | 0.00 | 0.00 | 0.00 | 3.9% | Y/N |
| LINDANE | 0.02 | 0.02 | 0.02 | 9.2% | Y/Y |

No blank samples showed traces of any parameters.

## Polychlorinated Biphenyls and Pesticides Analytical Recovery Determination

A spike recovery determination was made to evaluate both the analytical recovery of the laboratory, and to evaluate the 144 hour sampling procedure as to sampling loss.  A standard was obtained from the laboratory, and an aliquot added to each of two PUF plugs.  One was then stored for submission to the laboratory, while the second was treated as any other 144 hour sample.  Results obtained from these determinations yielded results that were within ±10% of the expected values, demonstrating the efficiency of the determination.

**Table 11: PCB Spike Recoveries (uG)**

| Parameter Name | uG/PUF | Blank | Blank/ug/PUF | Spike | Sample | Net | Net/ug/PUF |
|---|---|---|---|---|---|---|---|
| Total PCBs | 4 | 4 | 100.0% | 4 | 0.31 | 3.69 | 92.3% |

### Polar Organic Compounds, Carbonyl Data Completeness

Project completeness with reference to carbonyls is documented in the following table.  In this table, Completeness is the ratio of Ambient samples collected to total Sampling days.  The following table documents analytical completeness in terms of results obtained for samples submitted.   A new sampler was installed in September 1995.

**Table 12: Carbonyl Completeness**

| Sampling Completeness | Samples | Void | Ambient | Blanks | Co-Located | Duplicates | Samping Days |
|---|---|---|---|---|---|---|---|
| 93.3% | 43 | 3 | 28 | 4 | 3 | 4 | 30 |

| Analytical Completeness | Samples | Ambient | Blanks | Co-Located | Duplicates | Samples Submitted |
|---|---|---|---|---|---|---|
| 102.5% | 41 | 31 | 4 | 2 | 4 | 40 |

## Polar Organic Compounds, Carbonyl Analytical Results

Results for aldehyde analysis of all samples are presented in the following table. All values are in ug/m$^3$.

**Table 13: Carbonyl Results (ug/m$^3$)**

| Parameter | Average | Maximum | Minimum | %RSD | Detects | Reported |
|---|---|---|---|---|---|---|
| ACETALDEHYDE | 1.38 | 4.15 | 0.12 | 72.2% | 41 | 41 |
| ACETONE | 2.39 | 8.72 | 0.21 | 74.8% | 35 | 35 |
| FORMALDEHYDE | 1.62 | 18.45 | 0.11 | 187.7% | 38 | 41 |

## Polar Organic Compounds, Carbonyl Quality Assurance Parameters

Quality control data generated in the course of aldehyde sampling is documented in the following tables. The first table shows the results of all duplicate sample pairs, along with their averages and each set□s percent difference from the average. It should be noted that the first two data pairs for each parameter represent co-located samples obtained as a comparison between the old and new samplers.

With two exceptions, all duplicates are within ±25%. Both exceptions occur with the first co-located samples. The average percent difference between all data pairs is 15.7%. There were no bad data pairs

**Table 14: Carbonyl Duplicates (ug/m$^3$)**

| Parameter | Date | Primary | Duplicate | Average | % Diff | Detects |
|---|---|---|---|---|---|---|
| ACETALDEHYDE | 9/12/95 | 3.17 | 2.28 | 2.73 | 32.9% | Y/Y |
| ACETALDEHYDE | 9/27/95 | 2.64 | 2.08 | 2.36 | 23.8% | Y/Y |
| ACETALDEHYDE | 12/17/95 | 4.15 | 3.61 | 3.88 | 14.1% | Y/Y |
| ACETALDEHYDE | 2/15/96 | 1.22 | 1.13 | 1.18 | 7.5% | Y/Y |
| ACETALDEHYDE | 5/21/96 | 0.18 | 0.20 | 0.19 | 10.1% | Y/Y |
| ACETONE | 9/12/95 | 4.96 | 3.47 | 4.21 | 35.4% | Y/Y |
| ACETONE | 9/27/95 | 4.55 | 4.50 | 4.52 | 1.3% | Y/Y |
| ACETONE | 12/17/95 | 4.15 | 3.34 | 3.75 | 21.7% | Y/Y |

# Green Bay Urban Air Toxics

## Carbonyl Duplicates
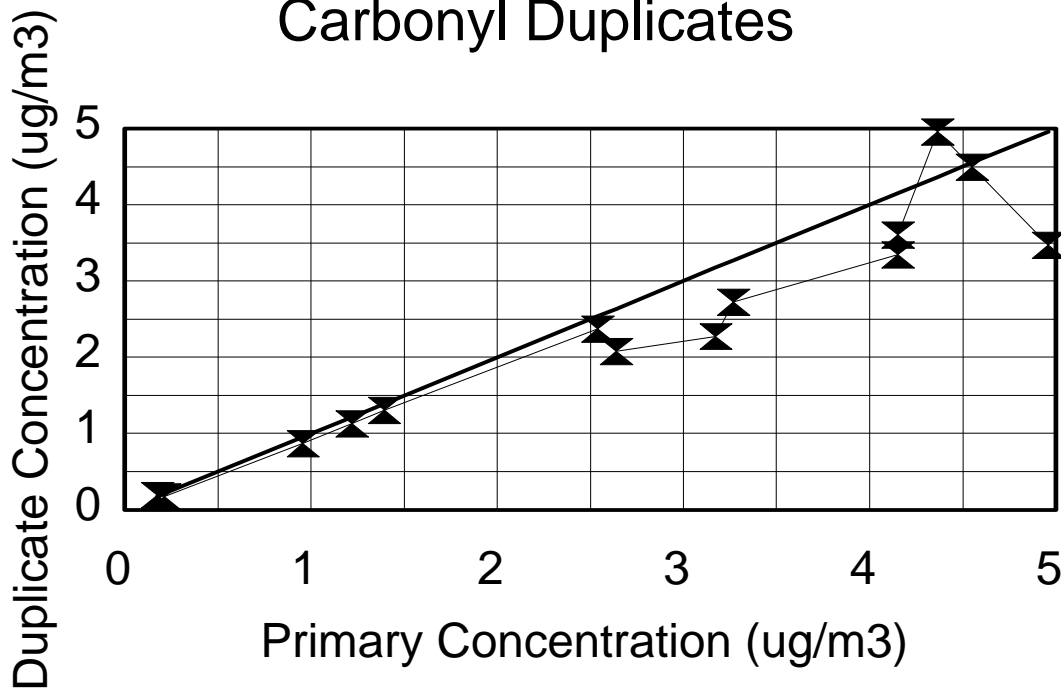


| ACETONE | 2/15/96 | 1.39 | 1.31 | 1.35 | 6.6% | Y/Y |
|---|---|---|---|---|---|---|
| FORMALDEHYDE | 9/12/95 | 4.36 | 4.95 | 4.66 | 12.6% | Y/Y |
| FORMALDEHYDE | 9/27/95 | 2.54 | 2.38 | 2.46 | 6.7% | Y/Y |
| FORMALDEHYDE | 12/17/95 | 3.27 | 2.73 | 3.00 | 18.1% | Y/Y |
| FORMALDEHYDE | 2/15/96 | 0.96 | 0.87 | 0.91 | 9.7% | Y/Y |
| FORMALDEHYDE | 5/21/96 | 0.21 | 0.18 | 0.20 | 19.0% | Y/Y |

The table below presents results from the blanks which have shown traces of different parameters.  These detects have been evaluated a typical sampling volume (1.05 $m^3$) to determine the level of potential interference.  A ⬜<=⬜ sign indicates interference which may or may not be related to the parameter in question.

**Table 15: Carbonyls in Blanks**

| Parameter | Date | ug/sample | ug/M3 |
|---|---|---|---|
| ACETALDEHYDE | 07/14/95 | 1.6 | 1.524 |
| ACETALDEHYDE | 10/06/95 | 0.015 | 0.014 |
| ACETALDEHYDE | 01/22/96 | 0.5 | 0.476 |
| ACETALDEHYDE | 04/15/96 | 0.29 | 0.276 |
| ACETONE | 07/14/95 | <=0.25 | <=0.238 |
| ACETONE | 10/06/95 | 0.44 | 0.419 |
| ACETONE | 01/22/96 | <=0.24 | <=0.228 |

| | | | |
|---|---|---|---|
| **ACETONE** | 04/15/96 | 0.51 | 0.486 |
| **FORMALDEHYDE** | 07/14/95 | <=0.13 | <=0.124 |

## Volatile Organic Compounds, Data Completeness

Project completeness with reference to VOCs is documented in the following table. Sampling Completeness is the ratio of Ambient samples collected to total Sampling days. Analytical Completeness in this table is the ratio of Samples to Samples Submitted.

**Table 16: VOC Completeness**

| Sampling Completeness | Samples | Voids | Ambient | Duplicates | Sampling Days |
|---|---|---|---|---|---|
| 96.7% | 38 | 4 | 29 | 5 | 30 |
| **Analytical Completeness** | **Samples** | **Ambient** | **Duplicates** | | **Samples Submitted** |
| 94.1% | 32 | 29 | 3 | | 34 |

## Volatile Organic Hydrocarbons, Toxics Analytical Results

The table following presents a summation of Toxics VOC data. Evaluation criteria are average, maximum, and minimum reported values, along with percent relative standard deviation. It should be noted that most non-detects are not included in these evaluations, as such results frequently were not incorporated into the database. Additional reporting criteria include the number of detects, and how many samples reported each particular parameter. Values are reported as ppbv.

**Table 17: Toxics VOC Results (ppbv)**

| Parameter Name | Average | Maximum | Minimum | %RSD | Detected | % Detection |
|---|---|---|---|---|---|---|
| **ACETYLENE** | 3.2 | 7.3 | 0.9 | 60.4% | 16 | 50.0% |
| **TOLUENE** | 1.0 | 2.5 | 0.1 | 70.6% | 33 | 103.1% |
| **PROPENE** | 0.6 | 1.6 | 0.2 | 70.6% | 17 | 53.1% |
| **BENZENE** | 0.5 | 1.3 | 0.2 | 55.2% | 22 | 68.8% |
| **XYLENES (m & p)** | 0.4 | 1.3 | 0.1 | 77.0% | 31 | 96.9% |
| **1,1,1-TRICHLOROETHANE** | 0.2 | 0.4 | 0.1 | 27.4% | 32 | 100.0% |
| **METHYLCHLORIDE** | 0.2 | 0.2 | 0.2 | 0.0% | 2 | 6.3% |
| **1,1,2,2-TETRACHLOROETHANE** | 0.2 | | | | 1 | 3.1% |
| **o-XYLENE** | 0.2 | 0.5 | 0.1 | 62.3% | 28 | 87.5% |
| **ETHYLBENZENE** | 0.2 | 0.4 | 0.1 | 60.9% | 29 | 90.6% |
| **CHLOROFORM** | 0.1 | 0.7 | 0.1 | 90.2% | 21 | 65.6% |
| **STYRENE** | 0.1 | 0.2 | 0.1 | 35.4% | 3 | 9.4% |
| **1,3 BUTADIENE** | 0.1 | 0.2 | 0.1 | 34.0% | 9 | 28.1% |
| **n-OCTANE** | 0.1 | 0.1 | 0.1 | 0.0% | 7 | 21.9% |
| **TETRACHLOROETHENE** | 0.1 | 0.1 | 0.1 | 0.0% | 8 | 25.0% |
| **CHLOROETHANE** | 0.1 | 0.1 | 0.1 | 0.0% | 2 | 6.3% |

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| | | | | | | |
|---|---|---|---|---|---|---|
| **CARBON TETRACHLORIDE** | 0.1 | 0.1 | 0.1 | 0.0% | 29 | 90.6% |
| **TRICHLOROETHENE** | 0.1 | | | | 1 | 3.1% |
| **CUMENE (i-PROPYLBENZENE)** | 0.1 | | | | 1 | 3.1% |
| **1,4-DICHLOROBENZENE** | 0.1 | | | | 1 | 3.1% |

## Volatile Organic Hydrocarbons, PAMS Analytical Results

In addition to the toxics parameters reported, a number of the canister samples sent to BRC were analyzed for PAMS compounds also. Results from these analysis are reported in the tables below. The first of these includes the various hydrocarbons groups which are reported as totals, while the second includes all individual species detected. Please note that the units for PAMS analysis is ppbC, as opposed to ppbv. Parts per billion Carbon can be related to parts per billion by volume by dividing the ppbC results by the number of carbons present in the reported parameter. This convention is derived from the use of a single representative hydrocarbon to calibrate the instrument used in this analysis. Reporting in ppbC is useful in PAMS analysis since these units are consistent with those used for modeling studies.

### Table 18a: PAMS VOC Group Results

| Parameter Name | Average | Maximum | Minimum | %RSD | Detected | % Detection |
|---|---|---|---|---|---|---|
| **TOTAL NMHC** | 269.4 | 772.7 | 149.3 | 61.1% | 14 | 100.0% |
| **ALKANES** | 170.8 | 592.0 | 39.1 | 86.5% | 14 | 100.0% |
| **TOTAL UNIDENTIFIED** | 64.6 | 111.4 | 12.6 | 47.7% | 14 | 100.0% |
| **AROMATICS** | 21.1 | 67.5 | 6.9 | 70.3% | 14 | 100.0% |
| **OLEFINS** | 13.0 | 46.1 | 4.3 | 86.8% | 14 | 100.0% |

### Table 18b: PAMS VOC Species Results

| Parameter Name | Average | Maximum | Minimum | %RSD | Detected | % Detection |
|---|---|---|---|---|---|---|
| **N-HEXANE** | 103.0 | 368.1 | 1.4 | 99.6% | 14 | 100.0% |
| **METHYLCYCLOPENTANE** | 14.8 | 50.8 | 0.7 | 93.2% | 14 | 100.0% |
| **N-BUTANE** | 7.6 | 35.7 | 2.8 | 109.4% | 14 | 100.0% |
| **TOLUENE** | 7.2 | 31.1 | 2.8 | 98.9% | 14 | 100.0% |
| **i-PENTANE** | 6.6 | 26.7 | 2.4 | 89.2% | 14 | 100.0% |
| **PROPANE** | 6.3 | 19.9 | 2.5 | 71.5% | 14 | 100.0% |
| **ETHANE** | 6.0 | 12.5 | 2.6 | 41.3% | 14 | 100.0% |
| **3-METHYLPENTANE** | 5.4 | 18.4 | 0.9 | 90.9% | 14 | 100.0% |
| **ETHYLENE** | 4.0 | 12.5 | 0.8 | 80.5% | 14 | 100.0% |
| **ACETYLENE** | 3.8 | 14.0 | 0.6 | 95.9% | 14 | 100.0% |
| **XYLENES (m & p)** | 3.2 | 9.4 | 0.9 | 67.0% | 14 | 100.0% |

| | | | | | | |
|---|---|---|---|---|---|---|
| **n-PENTANE** | 2.8 | 8.6 | 1.3 | 62.0% | 14 | 100.0% |
| **BENZENE** | 2.7 | 7.4 | 1.2 | 61.4% | 14 | 100.0% |
| **2-METHYLPENTANE** | 2.2 | 6.7 | 1.0 | 65.3% | 14 | 100.0% |
| **2,2,4-TRIMETHYLPENTANE** | 2.1 | 6.6 | 0.7 | 68.0% | 14 | 100.0% |
| **1,2,4-TRIMETHYLBENZENE** | 1.9 | 4.2 | 0.3 | 53.0% | 13 | 92.9% |
| **3-METHYLHEXANE** | 1.8 | 3.4 | 0.5 | 51.5% | 14 | 100.0% |
| **i-BUTANE** | 1.5 | 6.0 | 0.8 | 83.5% | 14 | 100.0% |
| **PROPENE** | 1.4 | 3.9 | 0.5 | 73.6% | 14 | 100.0% |
| **o-XYLENE** | 1.4 | 3.5 | 0.4 | 58.8% | 14 | 100.0% |
| **p-ETHYLTOLUENE** | 1.3 | 3.0 | 0.4 | 47.4% | 13 | 92.9% |
| **ETHYLBENZENE** | 1.1 | 3.1 | 0.3 | 58.4% | 14 | 100.0% |
| **2,3-DIMETHYLPENTANE** | 1.1 | 3.8 | 0.3 | 75.6% | 14 | 100.0% |
| **o-ETHYLTOLUENE** | 0.9 | 1.5 | 0.4 | 35.3% | 7 | 50.0% |
| **2-METHYLHEXANE** | 0.9 | 2.6 | 0.2 | 67.4% | 14 | 100.0% |
| **1,3,5-TRIMETHYLBENZENE** | 0.9 | 1.7 | 0.2 | 53.7% | 13 | 92.9% |
| **n-HEPTANE** | 0.8 | 2.4 | 0.4 | 65.8% | 14 | 100.0% |
| **m-ETHYLTOLUENE** | 0.8 | 1.4 | 0.2 | 40.1% | 13 | 92.9% |
| **n-NONANE** | 0.8 | 1.7 | 0.2 | 51.6% | 14 | 100.0% |
| **i-BUTENE** | 0.7 | 1.7 | 0.3 | 58.9% | 13 | 92.9% |
| **2,4-DIMETHYLPENTANE** | 0.7 | 2.0 | 0.1 | 70.4% | 14 | 100.0% |
| **2,3,4-TRIMETHYLPENTANE** | 0.6 | 1.9 | 0.2 | 68.0% | 14 | 100.0% |
| **CYCLOHEXANE** | 0.6 | 1.9 | 0.3 | 85.4% | 8 | 57.1% |
| **2,3-DIMETHYLBUTANE** | 0.6 | 1.9 | 0.2 | 68.0% | 14 | 100.0% |
| **n-PROPYLBENZENE** | 0.6 | 0.9 | 0.1 | 43.4% | 13 | 92.9% |
| **2-METHYL-2-BUTENE** | 0.6 | 2.0 | 0.2 | 83.0% | 11 | 78.6% |
| **METHYLCYCLOHEXANE** | 0.6 | 1.4 | 0.3 | 59.4% | 14 | 100.0% |
| **2-METHYL-2-PENTENE** | 0.6 | 0.7 | 0.4 | 27.3% | 2 | 14.3% |
| **n-OCTANE** | 0.5 | 1.2 | 0.1 | 67.8% | 14 | 100.0% |
| **2,2-DIMETHYLBUTANE** | 0.5 | 1.5 | 0.2 | 73.6% | 13 | 92.9% |
| **2-METHYL-1-BUTENE** | 0.4 | 1.5 | 0.2 | 81.4% | 11 | 78.6% |
| **1-BUTENE** | 0.4 | 0.8 | 0.2 | 53.8% | 7 | 50.0% |
| **trans-2-PENTENE** | 0.4 | 1.4 | 0.2 | 72.6% | 12 | 85.7% |
| **2,4-DIMETHYLHEXANE** | 0.4 | 1.0 | 0.1 | 53.8% | 11 | 78.6% |
| **ISOPRENE** | 0.4 | 0.8 | 0.1 | 50.0% | 10 | 71.4% |
| **trans-2-HEXENE** | 0.4 | 1.1 | 0.2 | 88.0% | 5 | 35.7% |
| **1-PENTENE** | 0.4 | 1.1 | 0.1 | 74.6% | 8 | 57.1% |
| **2-METHYLHEPTANE** | 0.4 | 1.1 | 0.1 | 60.9% | 14 | 100.0% |
| **3-ETHYLHEXANE** | 0.4 | 1.2 | 0.1 | 72.3% | 14 | 100.0% |
| **CYCLOPENTENE** | 0.3 | 1.3 | 0.1 | 141.2% | 5 | 35.7% |
| **CYCLOPENTANE** | 0.3 | 1.1 | 0.1 | 71.3% | 14 | 100.0% |
| **trans-2-BUTENE** | 0.3 | 0.9 | 0.1 | 75.0% | 8 | 57.1% |
| **2,4,4-TRIMETHYL-1-PENTENE** | 0.3 | 0.6 | 0.2 | 50.4% | 4 | 28.6% |
| **2,5-DIMETHYLHEXANE** | 0.3 | 0.9 | 0.1 | 74.9% | 11 | 78.6% |
| **CUMENE** | 0.3 | 0.3 | 0.3 | 0.0% | 3 | 21.4% |
| **2,3-DIMETHYLHEXANE** | 0.3 | 0.7 | 0.2 | 47.4% | 11 | 78.6% |
| **cis-2-PENTENE** | 0.3 | 1.2 | 0.1 | 106.8% | 11 | 78.6% |

| | | | | | | |
|---|---|---|---|---|---|---|
| cis-2-BUTENE | 0.3 | 0.6 | 0.1 | 71.3% | 5 | 35.7% |
| 1,3 BUTADIENE | 0.2 | 0.9 | 0.1 | 98.1% | 13 | 92.9% |
| 1-HEXENE | 0.2 | 0.3 | 0.2 | 20.2% | 3 | 21.4% |
| 3-METHYL-1-BUTENE | 0.2 | 0.3 | 0.1 | 47.4% | 4 | 28.6% |
| 2-METHYL-1-PENTENE | 0.2 | 0.3 | 0.1 | 56.6% | 3 | 21.4% |
| cis-2-HEXENE | 0.2 | 0.2 | 0.1 | 33.3% | 2 | 14.3% |

It should be noted that the hexane values obtained from these results are most likely an artifact from the use of this solvent during PUF sample preparation. There was a significant increase in the amount of this background through the testing period. The cause for this was investigated, and a leak was found in the outlet of the solvent hood located inside the sample site. This leak was then repaired, however PAMS analysis of these samples was not continued following this time, so that the effect of the repair is not known. The table below documents the impact of the hexane artifact through a comparison of TNMOC and hexane.

**Table 19: TNMOC With and Without Hexane (ppbc)**

| | Average | Maximum | Minimum | % RSD |
|---|---|---|---|---|
| MOC | 269.4 | 772.7 | 149.3 | 61.1% |
| MOC-Hex | 166.5 | 404.6 | 77.3 | 47.7% |
| % Hexane | 35.5% | 64.3% | 5.9% | 19.7% |

The PAMS analysis performed on these samples allows a comparison with similar results obtained from the official PAMS monitoring sites in southeast Wisconsin. The tables below show the total non-methane organic hydrocarbon concentrations and the top ten species from all PAMS sites plus Green Bay. Note that the Green Bay average Total NMOC is significantly higher than that of the other sites. Green Bay, like Milwaukee, is urban, however Green Bay is not under the control strategies enforced in Milwaukee to alleviate the ozone problem. The number in parenthesis following the site name represents the number of samples collected at each site.

**Table 20: TNMOC Comparison between PAMS and Toxics Sites (ppbc)**

| otal NMOC Comparison | Maximum | Average |
|---|---|---|
| Milwaukee (45) | 250 | 70.6 |
| Manitowoc (16) | 30 | 17.7 |
| Harrington Beach (15) | 39 | 24.4 |
| Green Bay (14) | 772.7 | 269.4 |
| Green Bay - Hexane | 404.6 | 166.5 |

The table below compares the top ten PAMS parameters observed at Green Bay with the same parameters from the PAMS sites. The columns labeled Rank indicate how these parameters compare with others in the other sites. It should be noted that the hexane values for Green Bay are disregarded for this comparison.

**Table 21: PAMS Parameter Comparison, PAMS and Toxics Sites (ppbc)**

| rameter Name | GB*[1] | UWM* | Rank | WD* | Rank | HB* | Rank |
|---|---|---|---|---|---|---|---|
| ETHYLCYCLOPENTANE | 14.8 | 0.9 | 20 | 0.0 | 26 | 0.1 | 27 |
| BUTANE | 7.6 | 5.4 | 4 | 1.1 | 5 | 1.1 | 6 |
| OLUENE | 7.2 | 4.7 | 5 | 1.3 | 4 | 1.6 | 4 |
| OPENTANE | 6.6 | 5.5 | 3 | 1.5 | 3 | 1.8 | 3 |
| ROPANE | 6.3 | 5.8 | 2 | 1.9 | 2 | 2.4 | 2 |
| THANE | 6.0 | 7.7 | 1 | 3.0 | 1 | 3.2 | 1 |
| METHYLPENTANE | 5.4 | 1.1 | 16 | 0.1 | 19 | 0.2 | 20 |
| THYLENE | 4.0 | 3.9 | 6 | 1.0 | 7 | 0.9 | 8 |
| CETYLENE | 3.8 | 3.9 | 7 | 0.8 | 8 | 0.9 | 7 |
| YLENES (m & p) | 3.2 | 2.8 | 8 | 0.7 | 11 | 0.7 | 11 |

## Volatile Organic Hydrocarbons, Passivated Canister Quality Assurance Parameters

Several methods of checking the quality of canister analysis are present with the data collected. First, there are several duplicate samples available. Secondly, there are several samples with two different analysis performed on them, each with some parameter overlap. This allows for an in depth determination of the validity of the results. The first graph below shows a comparison of duplicate samples analyzed for toxics parameters. A total of 111 data pairs are represented in this table, with 23 detect pairs (20.7%), and 4 unacceptable pairs (3.6%). Non-detect pairs show qualitative agreement and are not incorporated into the table. The average percent difference between the detect pairs is 4.8%. There are two detect pairs (1.8%) which fail the quality control limit of ±25%.

In addition to duplicate analysis of toxics parameters, there are also duplicate PAMS samples available for comparison. These results are summarized graphically on the following page. Out of a total of 150 data pairs, 94 are detect pairs (62.7%), 11 are unacceptable pairs (7.3%), and 36 show a greater than 25% difference (24.0%). The average percent difference is 25.5%.

As a final check on analysis, there are several parameters reported in both the toxics and the PAMS analysis. These results are graphed on the following page, and summarized by table on the second following page. It should be noted that PAMS ppbc values are converted to ppbv values by dividing the reported result by the number of carbon atoms in each parameter. Values represent averages over the number of samples analyzed.

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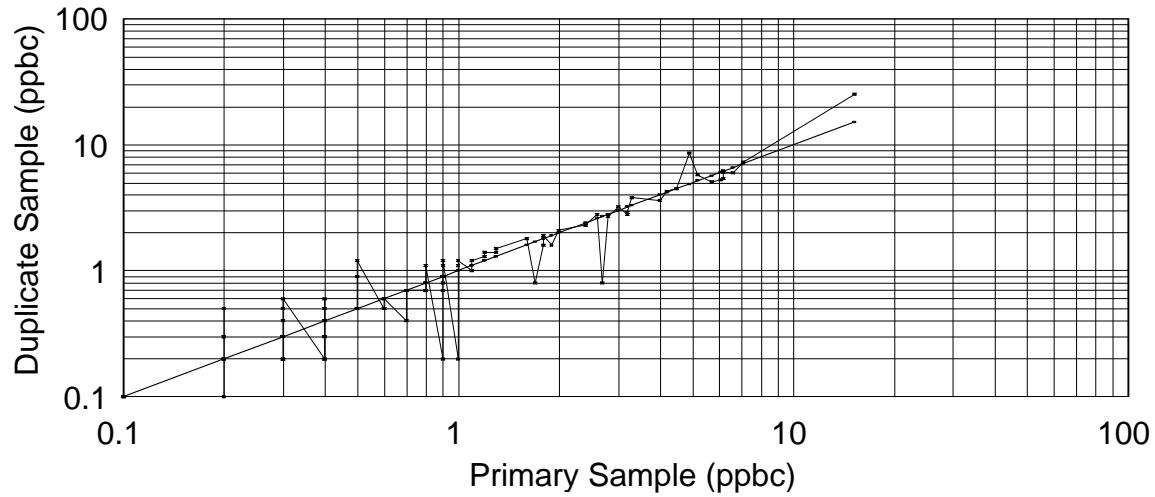[1]GB = Green Bay; UWM = Milwaukee; WD = Manitowoc; HB = Harrington Beach

# Green Bay Urban Air Toxics

## Toxic VOC Duplicate Samples
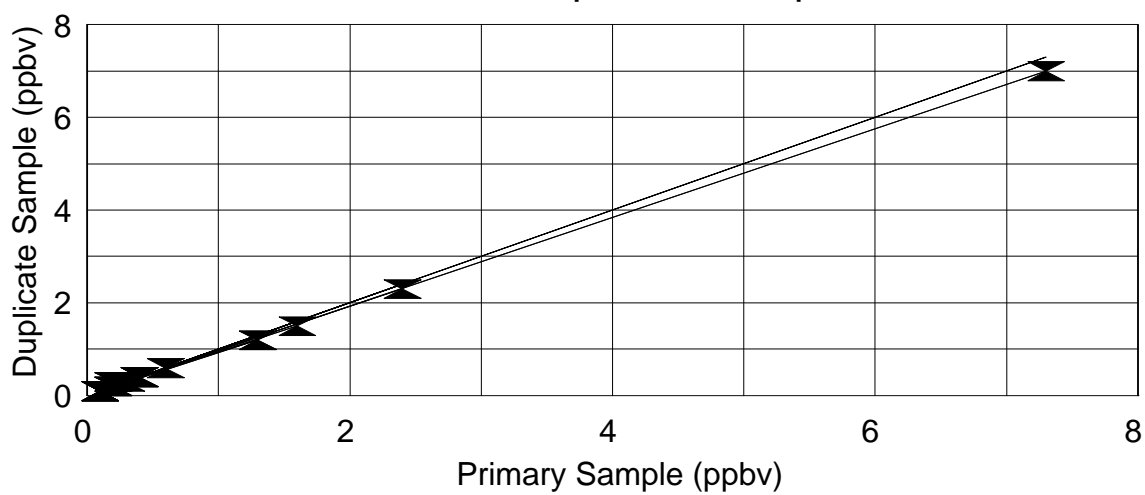
# Green Bay Urban Air Toxics

## PAMS VOC Duplicate Samples


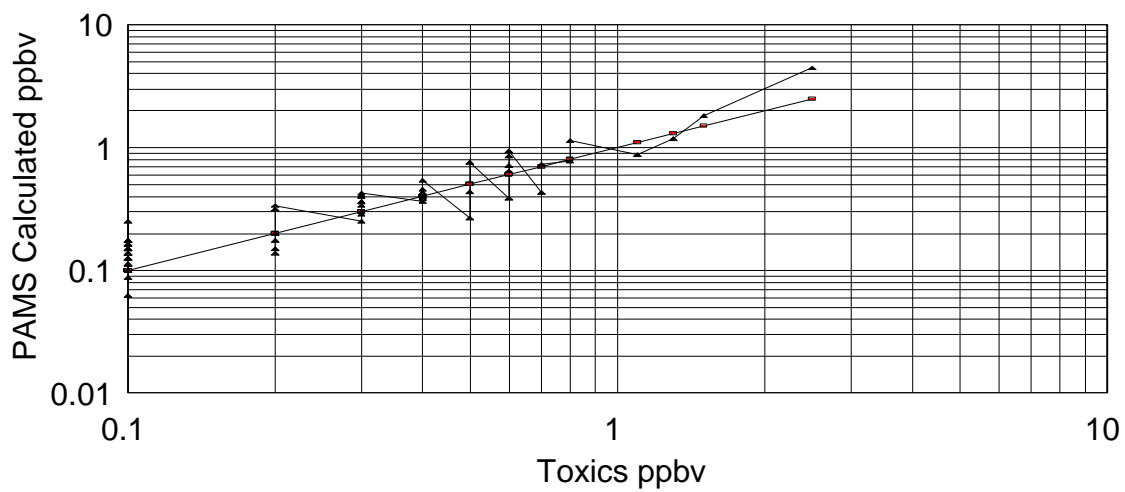
# Green Bay Urban Air Toxics

## PAMS/Toxic VOC Comparison

**Table 22: Toxics vs. PAMS Analysis (ppbv and calculated ppbv)**

| rameter | Toxics | PAMS | Average | % Difference | Samples |
|---|---|---|---|---|---|
| ENZENE | 0.36 | 0.36 | 0.36 | 0.9% | 5 |
| THYLBENZENE | 0.14 | 0.16 | 0.15 | 13.3% | 12 |
| OLUENE | 0.74 | 1.05 | 0.90 | 35.1% | 13 |
| YLENES (m & p) | 0.35 | 0.40 | 0.37 | 14.2% | 13 |
| XYLENE | 0.22 | 0.23 | 0.23 | 4.4% | 5 |

Analysis of field blanks has not been incorporated directly into the sampling scheme. Part of the analysis contract specifies that canisters be cleaned to <20 ppbc total, with individual target compounds present only at less than 0.2 ppb.

## INORGANIC PARAMETERS

## Total Suspended Particulate and Metals, Data Completeness

Project completeness with reference to TSP and metals is documented in the following table. In this table, Sampling Completeness is the ratio of Ambient samples collected to total Sampling days. Completeness in this table is the ratio of Samples to Samples Submitted.

**Table 23: TSP/Metals Completeness**

| ampling Completeness | Valid | Samples | Void | Sampling Days |
|---|---|---|---|---|
| 93.3% | 56 | 65 | 9 | 60 |

| nalytical Completeness | Analyzed | Valid Submitted | |
|---|---|---|---|
| 114.3% | 64 | 56 | |

## Total Suspended Particulate and Metals, Analytical Results

Results for TSPand metals analysis of all samples are presented in the following table. Values reported are in ug/M$^3$. Averages, maxima, minima and %relative standard deviations are shown. Please note that the Cadmium and Lead maxima are the highest values observed in Green Bay since the inception of toxics monitoring in 1991. The values were obtained on separate days, and so do not represent a single event.

**Table 24: Metals and TSP Results (ng/m$^3$ and ug/m$^3$, respectively)**

| arameter Name | Average | Maximum | Minimum | %RSD | Samples | Detects | % Detection |
|---|---|---|---|---|---|---|---|
| RSENIC | 1.14 | 2.87 | 0.12 | 54.4% | 57 | 44 | 77.2% |
| ADMIUM | 0.77 | 20.17 | 0.12 | 342.3% | 56 | 56 | 100.0% |
| HROMIUM | 3.46 | 13.98 | 1.10 | 68.0% | 57 | 53 | 93.0% |
| EAD | 12.97 | 215.76 | 0.13 | 211.8% | 57 | 57 | 100.0% |
| ELENIUM | 1.12 | 3.02 | 0.46 | 65.0% | 57 | 30 | 52.6% |
| ANADIUM | 1.64 | 4.39 | 1.05 | 46.1% | 57 | 29 | 50.9% |
| P (ug/M3) | 47.44 | 130.68 | 10.82 | 59.7% | 61 | 61 | 100.0% |

## Total Suspended Particulate and Metals, Quality Assurance Parameters

Quality assurance parameters reported by the laboratory include a total of six filters analyzed in duplicate, two blank filters spiked with a standard solution, and 4 split samples spiked with the standard solution. The resultant concentration calculated for the spiked filters is 50 ug/Liter for arsenic, lead, and vanadium; 40 ug/L for chromium and selenium; and 4 ug/L for cadmium. Results from these samples are presented in the tables following. Please note that the data is in ug/Liter of solution. Common factors (dilution factor and sample volume) allow for the direct application of the percentage differences to general metals determinations.



Green Bay Urban Air Toxics
Metals Duplicate Analysis
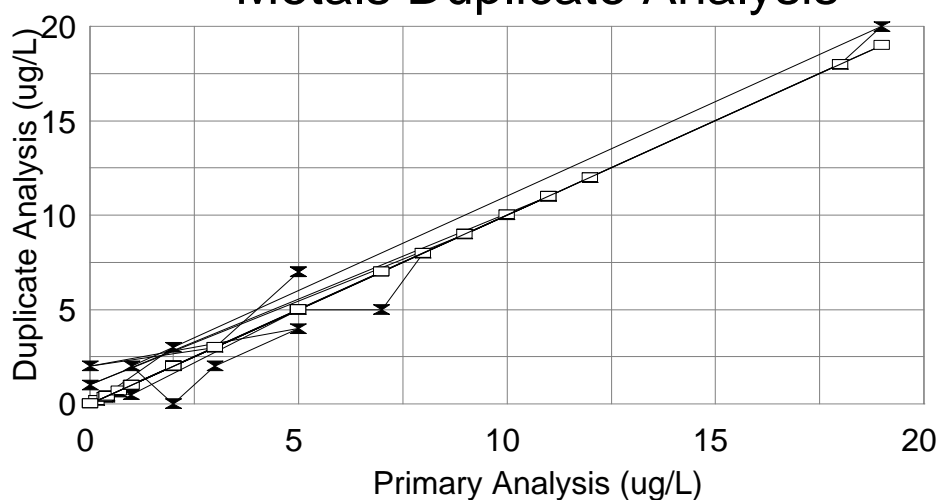
Duplicate analysis show a total of 36 data pairs, of which 11 (30.6%) are non-detect pairs with qualitative agreement. There are no bad pairs of data. Of the remaining 25 (69.4%) detect pairs, 6 (16.7%) show a greater than ± 25% difference. The overall average percent

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difference between duplicate analysis is 14.3%.

All spiked blank parameters are within ±10% of the expected values, with an average percent difference of 2.5%.

**Table 25: Laboratory Metals Spiked Blank Analysis (ug/L)**

| Parameter Name | Spike Level | Analysis | % Difference | Analysis | % Difference |
|---|---|---|---|---|---|
| ARSENIC | 50 | 51 | 2.0% | 51 | 2.0% |
| CADMIUM | 4 | 4.1 | 2.5% | 4.2 | 5.0% |
| CHROMIUM | 40 | 41 | 2.5% | 40 | 0.0% |
| LEAD | 50 | 50 | 0.0% | 52 | 4.0% |
| SELENIUM | 40 | 40 | 0.0% | 39 | 2.5% |
| VANADIUM | 50 | 50 | 0.0% | 55 | 10.0% |

Percent difference in the split spiked sample analysis involves adding the Spike Level (see table above) to the sample values, then subtracting the spiked values from the resultant values and dividing this result by the sample plus spike level value. Of the 24 data pairs, there are three bad data pairs (12.5%). In this case, bad data pairs are determined by Spiked values which are greater than the Spike Level, while the sample value is a non-detect. The overall average percent difference is 4.2% (including the bad data pairs), and all values except for one of the bad data pairs are within ±10%.

**Table 26: Laboratory Metals Split Spiked Sample Analysis (ug/L)**

| Parameter Name | Spiked | Sample | % Difference | Spiked | Sample | % Difference |
|---|---|---|---|---|---|---|
| ARSENIC | 51 | 1 | 0.0% | 54 | 2 | 4.0% |
| CADMIUM | 5.4 | 1.2 | 5.0% | 4.8 | 0.53 | 6.8% |
| CHROMIUM | 49 | 8 | 2.5% | 48 | 7 | 2.5% |
| LEAD | 82 | 30 | 4.0% | 72 | 20 | 4.0% |
| SELENIUM | 43 | 4 | 2.5% | 43 | 3 | 0.0% |
| VANADIUM | 55 | 4 | 2.0% | 53 | 3 | 0.0% |
| ARSENIC | 51 | 2 | 2.0% | 53 | ND | 6.0% |
| CADMIUM | 5.1 | 0.95 | 3.8% | 4.6 | 0.28 | 8.0% |
| CHROMIUM | 43 | 5 | 5.0% | 42 | 4 | 5.0% |
| LEAD | 66 | 17 | 2.0% | 66 | 19 | 6.0% |
| SELENIUM | 45 | 2 | 7.5% | 43 | ND | 7.5% |

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| VANADIUM | 50 | ND | 0.0% | 43 | ND | 14.0% |

# Evaluation

The toxics monitoring prototype site in Green Bay has continued to provide a significant quantity of information regarding a number of toxic compounds present in the air of this city.   Changes instituted during the 95/96 sampling season include altering parameter lists of PCBs and PAHs, changing the PCB winter sampling protocol and improving laboratory detection limits, and changing to a newer carbonyl sampler.

## Polynuclear Aromatic Hydrocarbons

This particular test shows some difficulties.  Studies in the literature indicate that sampling with a filter/PUF combination tends to lead to loss of the lighter compounds (2 and 3 rings; Napthalene, Phenanthrene, Anthracene).  Some initial investigations into the use of XAD resin as a backup to the PUF were made, with the goal being to obtain sampling material which passed the background test for all parameters tested.  This testing continued into the 1996/1997 sampling season and will be discussed further in the next report.  No ambient samples have been obtained using a combination sampling medium.

Blank sampling media concentrations of several parameters (Benz a Anthracene, Fluoranthene, Naphthalene, Phenanthrene and Pyrene) are frequently above the quality control target level of 10 ng.  In most cases, the observed levels translate to less than 10% of the average values, with Naphthalene as a notable exception to this, with blanks frequently as high as 50% or more of the average ambient values.

In addition to the poor blank quality and potential problems related to sampling media, duplicate precision with this test remains questionable.  Only 3 parameters (Anthracene, Benzo (a) Anthracene and Phenanthrene) have results which are consistently within the ± 15% QC goal.  Of these, Phenanthrene is the only parameter which was reported during the first four years of monitoring, during which it⬚s duplicate precision averaged ± 26.5%.  The implication of this is that there are serious problems either in sampling or at the laboratory.

A blind check of the laboratory was made through the preparation and submission of spiked samples for analysis.  Results of this check show relability for only a few of the parameters.  Overall, the spiking tests indicate difficulties in this determination both at the sampling (loss of more volatile compounds) and analytical phases (peak separation and identification difficulties). It should be noted, however, that several of the less volatile compounds did pass this test, thereby validating their data, at least on this level.  Anthracene is the only parameter which has passed all quality control criteria.

## Polychlorinated Biphenyls and Pesticides

Improvements instiued in the PCB and pesticide testing include altering the parameter list, lengthening winter sampling time and decreasing laboratory detection limit. The result of this is an increase in the detection rate, and a greater array of parameters quantified. Overall this makes this particular test the most improved over the course of this sampling season.

## Carbonyls

There has been little change in the carbonyl sampling from previous years. All sampling parameters were within ranges established in previous years. Addition of a new sampler did not alter procedures or results to a significant extent.

## VOCs

The VOC program proceeded much as established during 1994 and 1995. PAMS analysis of compounds was discontinued by the lab in December 1995, so that there remains a limited amount of data available for comparison with the Wisconsin PAMS sites. What little data there is, however, is provacative, as the totals encountered in Green Bay, even when accounting for site artifacts derived from semi-volatile organic sample preparation techniques, are consistently higher than values obtained from the other sites. This could be an indication of the value of reformulated gasoline and emissions testing in reducing ambient VOCs.

Toxic VOC parameters were quite similar to previous years, although there were new highs and higher averages for Acetylene and Toluene. Quality control parameters for the toxics analysis indicate that the data is acceptable.

## Non-Volatile Metals

Metals results from the 1995/1996 sampling season continue along the same lines as previous years, with the exception of new high values for Lead and Cadmium. Quality control parameters indicate the data is acceptable.

# Recommendations

Recommendations regarding continued operations and expansion of the toxics monitoring network fall into two basic categories: further refinements of methods, and expanding the network to different localities. Several of these changes are already being implemented as this report nears completion.

## Methodology Changes, PAHs

Sampling for PAHs was discontinued in January 1997 to be able to address some of the issues discussed in the Evaluation section above. These parameters are both potential health concerns and important markers for combustion sources. Improvements to the test are important to obtain reliable results. These improvements fall under three main areas. The first of these is in sampling. As our evidence from the spiking experiment confirms, lighter PAHs can be lost in the sampling process. As such further investigation into a combination or other alternative sampling material is vital.

The second main improvement involves a more focussed and detailed parameter list. PAHs are ubiquitous compounds with both natural and anthropogenic sources. Many studies have been conducted determining PAH fingerprints of different combustion sources. No single compound is necessarily indicative of a particular source, but rather ratios of different compounds are used. If PAH testing is to be re-instated, a parameter list specific and inclusive enough to allow for source analysis is required. This will allow us to indicate whether the PAHs are coming from diesel or gasoline engines, coal or wood combustion, and thus provide more complete information evaluate.

The third and perhaps most important improvement needs to be in the laboratory. Difficulties in sample recovery, compound identification and background contamination need to be addressed through basic developement work in the laboratory. A thorough evaluation of sample preparation and analysis is required, with institution of improvements assumed. Although the quality control problems we have seen over the years with this test can not realistically be placed entirely within the realm of the lab, there is significant evidence indicating that a potentially major portion of them are.

## Expanding the Toxics Monitoring Program

The original intention of the program was for the Green Bay site to serve as a prototype for a network composed of permanent sites in 4 or 5 cities around the state. The air toxics monitoring network is intended to collect data to provide information to be analyzed for potential health effects, trends and atmospheric chemistry. The prototype site in Green Bay has the additional purpose of evaluating various sampling and analytical methodologies.

Our work at Green Bay has shown that we can obtain reliable data for PCBs, pesticides, polar organic compounds, volatile organic compounds and non-volatile metals. This data can be used to determine potential health effects of exposure to the ambient air and to provide a baseline for evaluation of future trends in the concentration of these materials.

The methods used for these parameters are available to be deployed either at full or partial toxic sites. Such sites can be either permanent and fixed with their own power supply, or temporary using portable power and sampling units, as required for meeting requests for information on air quality around the state.

Monitoring these trace elements and compounds in the atmosphere remains an important aspect of understanding the effect industrial culture has on our ecosystem. Comparison of rural and urban sites from around the state will provide clearer information for evaluating potential health effects and contaminant trends in the atmosphere, in addition to imperative information regarding transport and other issues.

As such, there are several options for how to proceed from here with the Toxics Monitoring program, both in Green Bay and beyond. In general, these options all involve some level of continued monitoring in Green Bay, plus the addition of more sites. The spectrum of options ranges from maintaining a full permanent site in Green Bay (optionally moving it to another city) in addition to an aggressive rotational sampling program using existing TSP sites and portable samplers, to a cut back program involving no fixed sites and minimal rotational sampling.

Potential sites could include Milwaukee (Menominee Valley), Superior, Wausau, Eau Claire, Madison, Janesville, La Crosse, Beloit or another of the Fox Valley cities for urban industrial areas. Trout Lake would be an ideal site for a rural area. Specific locations to be used will be worked out with all interested parties.

Metals and carbonyl sampling at the Green Bay site was cut back to once every 30 days beginning in July 1996. At the same time, once per 30 days metals samples were collected from existing TSP sites in Superior, Milwaukee and Trout Lake. This statewide metals sampling is an important step to furthering our understanding of these pollutants on a wider basis, and should be continued if at all possible.

VOC data from Green Bay has been affected by several factors, leading to less data than the metals or carbonyls. The primary factor leading to this state of affairs is the sampling down time during the introduction of stainless steel canisters. There is currently a minimum of data present for a baseline evaluation. If the site remains in Green Bay, it is recommended that VOC sampling and analysis be continued at the current level for at least another year to generate further data for future trends analysis.

PCB and pesticide sampling has been difficult. It is only in the past year that year round results have been obtained. As such, there is not yet enough data to analyze seasonal or yearly trends of these materials in the urban atmosphere. With plans in the works to clean up the Fox river through removal of contaminated sediment, the potential for releasing additional PCBs to the atmosphere provide additional incentive to maintain a PCB presence in Green Bay.

Sampling frequency for PCBs during the 1996/1997 sampling season were altered. Two periods of intensive (one in every six day) sampling were included in an attempt to capture data that will aid in determining whether there is a wind direction correlation to the concentrations observed. Further refinement of this type of scheduling is recommended.

With the information currently in hand, there is a generally good characterization of toxics in Green Bay□s air. As such it is strongly recommended that alternate sites be investigated for further enhancing our understanding of toxics in Wisconsin□s urban air, and to provide data for

evaluating the health risks associated with them.

**References**

DNR Air Monitoring Handbook

Green Bay Urban Air Toxics Monitoring, A Summary Report for the Period July 1991 - June 1995, PUBL-AM-218-97, State of Wisconsin, Department of Natural Resources, 2/97